

## PHOTOCATALYST SYSTEM

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## Abstract of JP2003210998

PROBLEM TO BE SOLVED: To provide a photocatalyst system developing photocatalytic effect by the irradiation with light of a visible light region (wavelength: 420 nm or more) or an infrared region (wavelength: 750 nm or more).

SOLUTION: The photocatalyst system operated within a visible light/infrared region is assembled by combining a photocatalyst using light of an ultraviolet region heretofore with an up-conversion material being a material for converting visible light/infrared rays to ultraviolet rays/visible light. That is, the photocatalyst system comprises the photocatalyst and the up-conversion material.

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the photocatalyst system which has a photocatalyst effect by the exposure of visible light or infrared light in details more about a photocatalyst system.

[0002]

[Description of the Prior Art] In order to carry out the catalyst of the chemical reaction by making sunlight into an energy source, many photocatalyst materials are developed and the some are already put in practical use. The photocatalyst these-put in practical use is mainly using titanium oxide as the main ingredients, therefore mainly uses the ultraviolet radiation portion with low intensity among sunlight. Although the catalyst material which can use visible light with larger intensity in sunlight is also developed, they have toxicity and a fault of the material itself denaturalizing quickly working, and it has not resulted in utilization. The photocatalyst material which causes catalytic reaction by the optical exposure of an infrared light field has not been found out yet.

[0003] In order to carry out the catalyst of the chemical reaction by making sunlight into an energy source in recent years, many photocatalyst materials are developed and there are titanium oxide, a cadmium sulfide, zinc sulfide, etc. in them ("catalyst chemicals with which light is concerned" chemicals total theory No.23, and edited by Chemical Society of Japan (1994)). Among these, what used titanium oxide as the main ingredients is already put in practical use as an antibacterial tile, an odor removal filter, etc. (the newest photocatalyst art, N tea S (2000)). As for the wavelength of the light which the band gap is 3.0 - 3.2 eV, and can use titanium oxide, the ultraviolet radiation portion below about 400 nm has mainly become. Therefore, when using these practical use catalyst, the ultraviolet rays of a slight quantity contained in sunlight or a fluorescent lamp, the black light which takes out only ultraviolet rays, etc. are used. These days, there is still room in using the visible light whole region which occupies most portion of sunlight of that (1997) by which the titanium oxide system photocatalyst in which this absorption end was prolonged to the 500 nm neighborhood of a light range is also developed (Yamashita, security, chemicals, and 52 and 74) as a result of various improvement. The band gap of a cadmium sulfide, zinc sulfide, etc. which are known as a catalyst with a visible optical response is about 2.4 eV. The light which can be used is as follows [ the about 550 wavelength nm ], and, similarly has not come (as the photocatalyst with these visible optical responses was mentioned above, utilization is not carried out for degradation [ toxicity or use ] ) to use the whole region of visible light. [ the ] The catalyst which causes catalytic reaction in an infrared light field (wavelength. more than 750 nm) has not been found out yet.

[0004] On the other hand, the rise conversion art of changing incident light into the outputted ray of short wavelength is known (Tanabe, Hirao, Toratani, solid physics, 27, and 186 (1992)). Using the energy level of the rare earth ions doped in a crystal or glass, it can be visible, or can change into ultraviolet radiation, the photon of two or more long wavelength can participate near-infrared excitation light in excitation efficiently, and this can emit a visible or ultraviolet ray light of short wavelength. The rise conversion material of various combination is developed from such a viewpoint (JP,2000-339735,A, JP,9-208947,A, JP,9-86958,A, JP,7-162062,A, etc.).

[0005]

[Problem(s) to be Solved by the Invention] An object of this invention is to provide the catalyst system which has a photocatalyst effect by the exposure of the light of a light range (wavelength. more than 420 nm) or an infrared light field (wavelength. more than 750 nm). This invention is the infrared light field which was not used the light range where intensity is higher, and until now, and enables it to use stably and safely the photocatalyst which was using conventionally the light of the ultraviolet region where intensity is low among sunlight.

[0006]

[Means for Solving the Problem] . In this invention, it is already used in a partial area of ultraviolet radiation and visible light, and the performance in use is established. Or a photocatalytic system which operates a photocatalyst in which it turns out that high performance is shown in a partial area of visible light near ultraviolet radiation and ultraviolet radiation in visible and an infrared light field combining rise conversion material which is the material which changes visible and infrared light into ultraviolet and visible light according to a multiphoton process was assembled.

[0007] That is, this invention is a photocatalyst system which comprises a photocatalyst and rise conversion material. This photocatalyst Titanium oxide, strontium titanate, metal salt of tantalum acid, It is what uses as the main ingredients at least one sort chosen from tantalum oxide, zirconium oxide, and a group that comprises metal salt of niobic acid, It is preferred for this rise conversion material to use as the main ingredients at least one sort chosen from a group which comprises aluminum fluoride and indium fluoridation, zinc fluoride, a germanium dioxide, and tellurium oxide, and to make this contain a rare earth element. This photocatalyst may also contain a co-catalyst further.

[0008]

[Embodiment of the Invention] The photocatalyst used by this invention is a material which carries out the catalyst of the chemical reaction on the surface by irradiating with light, Titanium oxide, strontium titanate, the potassium of tantalum acid, sodium, It is salts, such as salts, such as barium, tantalum oxide, zirconium oxide, potassium of niobic acid, and a rubidium, and co-catalysts (Pt, RuO<sub>2</sub>, Rh, NiO<sub>x</sub> (x expresses the number which becomes settled in the valence of nickel.), CeO<sub>2</sub>, etc.) may be added to this. As this catalyst, titanium oxide is preferred, and Pt is preferred as a co-catalyst. Although the weight of the co-catalyst to a photocatalyst should just be the usual catalyst amount, 0.1 to 1.0 % of the weight is preferred.

[0009] Rise conversion material is the material which will emit the light of wavelength shorter than incident light according to a multiphoton process if this is excited by light, The AlF<sub>3</sub> system which uses aluminum fluoride as the main ingredients, the InF<sub>3</sub> system which uses indium fluoridation as the main ingredients, The ZnF<sub>2</sub> system which uses zinc fluoride as the main ingredients, the GeO<sub>2</sub> system which uses a germanium dioxide as the main ingredients, Tellurium oxide on glass, such as a TeO<sub>2</sub> system used as the main ingredients, Eu, Rare earth elements, such as Ho, Er, and Tm, are made to contain. For example (49-y), AlF<sub>3</sub>, yAlPO<sub>4</sub>, 1EuF<sub>3</sub>, 30CaF<sub>2</sub>, and 20BaF<sub>2</sub> (y=0-20), 40AlF<sub>3</sub>, 22CaF<sub>2</sub>, 22BaF<sub>2</sub>, 15YF<sub>3</sub>, and 1ErF<sub>3</sub>, 40AlF<sub>3</sub>, 22CaF<sub>2</sub>, 22BaF<sub>2</sub>, 15YF<sub>3</sub>, and 1TmF<sub>3</sub>, 99.9 (38InF<sub>3</sub>, 19BaF<sub>2</sub> and 19ZnF<sub>2</sub>, 10PbF<sub>2</sub>, 10SrF<sub>2</sub>, 2AlF<sub>3</sub>, and 2GdF<sub>3</sub>) and 0.1TmF<sub>3</sub>, 99.9 (38InF<sub>3</sub>, 18BaF<sub>2</sub>, 19ZnF<sub>2</sub> and 10PbF<sub>2</sub>, 9SrF<sub>2</sub>, 2AlF<sub>3</sub>, 2GdF<sub>3</sub>, and 2YbF<sub>3</sub>) and 0.1TmF<sub>3</sub>, 99.9 (40ZnF<sub>2</sub>, 15AlF<sub>3</sub> and 15BaF<sub>2</sub>, 15SrF<sub>2</sub>, and 15YF<sub>3</sub>) and 0.1TmF<sub>3</sub>, 99.9 (60ZrF<sub>4</sub>, 33BaF<sub>2</sub>, and 7LaF<sub>3</sub>) and 0.1TmF<sub>3</sub>, 99.9 (60GeO<sub>2</sub>, 30BaO, and 10ZnO) and 0.1TmO<sub>1.5</sub>, 99.9 (60TeO<sub>2</sub>, 30BaO, and 10ZnO) and 0.1TmO<sub>1.5</sub>, 95 (38InF<sub>3</sub>, 19BaF<sub>2</sub> and 19ZnF<sub>2</sub>, 10PbF<sub>2</sub>, 10SrF<sub>2</sub>, 2AlF<sub>3</sub>, and 2GdF<sub>3</sub>) and 5EuF<sub>3</sub>, 95 (38InF<sub>3</sub>, 18BaF<sub>2</sub>, 19ZnF<sub>2</sub> and 10PbF<sub>2</sub>, 9SrF<sub>2</sub>, 2AlF<sub>3</sub>, 2GdF<sub>3</sub>, and 2YbF<sub>3</sub>) and 5EuF<sub>3</sub>, 95 (40ZnF<sub>2</sub>, 15AlF<sub>3</sub> and 15BaF<sub>2</sub>, 15SrF<sub>2</sub>, and 15YF<sub>3</sub>) and 5EuF<sub>3</sub>, 95 (60ZrF<sub>4</sub>, 33BaF<sub>2</sub>, and 7LaF<sub>3</sub>) and 5EuF<sub>3</sub>, 95 (60GeO<sub>2</sub>, 30BaO, and 10ZnO) and 5EuO<sub>1.5</sub>, 95 (60TeO<sub>2</sub>, 30BaO, and 10ZnO), 5EuO<sub>1.5</sub>, etc. are mentioned (Tanabe, Hirao, Toratani, solid physics, 27, and 186 (1992)).

[0010] the content ratio of a rare earth element [ on rise conversion material and as opposed to glass, such as an AlF<sub>3</sub> system, an InF<sub>3</sub> system, a ZnF<sub>2</sub> system, a GeO<sub>2</sub> system, or a TeO<sub>2</sub> system, ] -- 0.01-50-mol % -- it is 0.1-10-mol % preferably, although the weight ratio of rise conversion material to a photocatalyst does not have restriction in particular -- desirable -- 0.1-10 -- it is 0.5-2.0 more preferably.

[0011] The role of the rise conversion material in this invention absorbs the light (visible light and infrared light of long wavelength) of the low energy which cannot be exploited with the photocatalyst material itself, changes it into energy-rich ultraviolet radiation or the visible light of short wavelength, and emits light in this. For this reason, inside rise conversion material, 2 or 3 photons of the visible light of low energy or infrared light are absorbed, and one photon of high energy is emitted more. A photocatalyst completes a photocatalysis in response to ultraviolet [ from this rise conversion material ] , or visible photoluminescence in the photocatalyst system of this invention.

[0012] In the photocatalyst system of this invention, a photocatalyst material and the rise conversion material should just be in the structure and physical relationship which can exchange light, and both may take powder, colloid, a thin film, and what kind of other shape. Such a system can be constituted as follows, for example.

- 1) Atomize a catalyst material and each rise conversion material, mix, and use as a photocatalyst material as it is (the method of atomization and mixing is not asked.).
- 2) Make a photocatalyst material and rise conversion material both suspended to solvents, such as water, and use as a photocatalyst (the kind of solvent and the method of suspension are not asked.).
- 3) Distribute another side using a sol gel process etc. in the material matrix of either a photocatalyst material or rise conversion material (the method of distribution is not asked.).
- 4) Distribute and support the particles of another side on the surface of either a photocatalyst material or rise conversion material (the method of distribution and support is not asked.).

[0013] When rise conversion material is atomized, the excitation light enhancement by particle laser oscillation may take place, and the effect over the performance of the photocatalytic system of this is also included in this invention concept. Namely, when rise conversion material is atomized, The case where the enhancement spontaneous emission or laser oscillation in which luminescence intensity increases by what is called optical Anderson localization happens is known, and when this occurs, luminescence of intensity higher than mere rise conversion can be obtained.

[0014]

[Effect of the Invention] By this invention, the photocatalyst which only the ultraviolet radiation whose intensity in sunlight is low until now has used can also use now visible light with larger intensity. It is expected that the infrared light (synchrotron radiation from sunlight, a high temperature furnace, etc.) which did not have use assumed as an energy source of a photocatalyst chemical reaction until now can also be used now. The following application can be considered in the photocatalyst system of this invention.

- 1) Make the photocatalyses (for example, prevention of removal of air pollution substances, such as disassembly of water, decomposition removal of an underwater organic pollutant, and nitrogen oxides (NO<sub>x</sub> etc.), an offensive odor, bacteria, contamination, etc., etc., etc.) which used ultraviolet radiation conventionally perform using visible light or infrared light.
- 2) Use as materials (for example, photocatalyst building materials etc. which have functions, such as a photocatalyst, wastewater cleaning material, air cleaning material, deodorization, antibacterial properties, antifouling) for making the above-mentioned reaction of 1 cause.
- 3) Use as an electrode material of a solar cell.

[0015]

[Example] Hereafter, although this invention is illustrated in the example, it does not mean limiting this invention.

In example 1, this example, the catalysis of the photocatalyst system of this invention in the nitrogen-oxides removal reaction in the atmosphere was investigated using various light sources. As a photocatalyst, the titanium oxide (TiO<sub>2</sub>) powder which hydrolyzed, and prepared and obtained titanic acid isopropoxide was used. As a rise conversion material, the thulium content aluminum fluoride system glass (40AlF<sub>3</sub>, 22CaF<sub>2</sub>, 22BaF<sub>2</sub>, 15YF<sub>3</sub> and 1TmF<sub>3</sub>) powder which carried out melting mixing, prepared each ingredient, and obtained it was used. It is a square-shaped coil made from quartz (the cross-section area of 1 cm) about what mixed each such photocatalyst powder and 0.1g of powder of rise conversion material. [ 2 and ] It installed in a pars basilaris ossis occipitalis 10 cm in length, and the air which contains 1 ppm of nitric oxide (NO) in this at a room temperature was circulated by 0.2-1./, from the coil upper part, it irradiated with 200W xenon lamp light, and the wavelength selection filter was suitably installed between this coil and a xenon lamp. Arrangement of each device in this examination is shown in drawing 1.

[0016] When it irradiates with a xenon lamp without using (2) filters, when not applying light at all as (1) control (it expresses "with no irradiation light".) (it expresses "a front light exposure"), an examination as (3) filters, 580 -- nm -- less than -- light -- transmissivity -- zero -- % -- it is -- and -- 630 -- nm -- more than -- light -- transmissivity -- 92 -- % -- it is -- a sharp cut filter -- letting it pass -- a xenon lamp -- light -- having glared -- a case (it expresses "the filter 1".) -- and -- (- four --) -- a filter -- \*\*\*\*\*". The transmissivity of light of 720 nm or less is 0%, and it carried out by being four kinds when the transmissivity of not less than 820-nm light irradiates with xenon lamp light through the sharp cut filter which is 90% (it expresses "the filter 2"). It measured by infrared absorption spectrometry by making the decrement of NO after an examination into conversion.

[0017] It measured like Example 1 except not using comparative example 1 rise conversion material. The measurement result of Example 1 and the comparative example 1 is shown in Table 1.

[Table 1]

|      | 反応率(%) |      |        |        |
|------|--------|------|--------|--------|
|      | 照射光なし  | 全光照射 | フィルター1 | フィルター2 |
| 実施例1 | 0      | 13   | 3.6    | 1.9    |
| 比較例1 | 0      | 14   | 0      | 0      |

[0018] In the comparative example 1, under an ultraviolet radiation exposure, a test reaction advances only with a photocatalyst ( $\text{TiO}_2$ ) (even if there is no rise conversion material), but by visible light or infrared light, it does not react at all. However, when rise conversion material was made to coexist with a photocatalyst in Example 1, the reaction of ultraviolet radiation advanced [ visible light or infrared light ] from the first.

[0019] In example 2 this example, the catalysis of the photocatalyst system of this invention in the decomposition reaction of the water which uses methanol as a sacrifice reagent was investigated using the same various light sources as Example 1. As a photocatalyst, the platinum support titanium oxide ( $\text{Pt/TiO}_2$ ) powder which carried out impregnating support and prepared platinum salts to titanium oxide of Example 1 was used. As a rise conversion material, Thulium content fluoridation indium system glass ( $38\text{InF}_3$ ,  $19\text{BaF}_2$ ,  $19\text{ZnF}_2$  and  $10\text{PbF}_3$  and  $10\text{SrF}_2$ ,  $2\text{AlF}_3$ ,  $2\text{GdF}_3$  and  $22\text{ZnF}_2$ , and  $0.1\text{TmF}_3$ ) powder. Melting mixing was carried out, and each ingredient was prepared, and was used. Such photocatalyst powder and 1 g of powder of rise conversion material were made suspended each in reaction mixture (methanol 10% solution), it irradiated there with xenon lamp light like Example 1, and the quantity of the hydrogen to generate was measured by gas chromatography.

[0020] It measured like Example 2 except not using comparative example 2 rise conversion material. The measurement result of Example 2 and the comparative example 2 is shown in Table 2.

[Table 2]

|      | 水素発生量 ( $\mu$ モル) |      |        |        |
|------|-------------------|------|--------|--------|
|      | 照射光なし             | 全光照射 | フィルター1 | フィルター2 |
| 実施例2 | 0                 | 612  | 25     | 5      |
| 比較例2 | 0                 | 816  | 0      | 0      |

In the comparative example 2, under an ultraviolet radiation exposure, a test reaction advances only with a photocatalyst ( $\text{Pt/TiO}_2$ ) (even if there is no rise conversion material), but by visible light or infrared light, it does not react at all. However, in Example 2, when rise conversion material was made to live together in a photocatalyst, the reaction of ultraviolet radiation advanced [ visible light or infrared light ] from the first.

[Claim 1] A photocatalyst system which comprises a photocatalyst and rise conversion material.

[Claim 2] Said photocatalyst Titanium oxide, strontium titanate, metal salt of tantallic acid, It is what uses as the main ingredients at least one sort chosen from tantalum oxide, zirconium oxide, and a group that comprises metal salt of niobic acid, The photocatalyst system according to claim 1 which said rise conversion material used [ photocatalyst system ] as the main ingredients at least one sort chosen from a group which comprises aluminum fluoride and indium fluoridation, zinc fluoride, a germanium dioxide, and tellurium oxide, and made this contain a rare earth element.

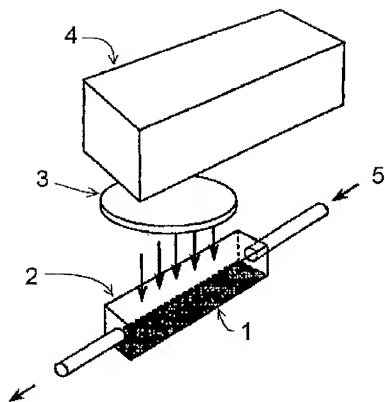
[Claim 3] The photocatalyst system according to claim 2 whose metal salt of said niobic acid metal salt of said tantallic acid is a salt of potassium of tantallic acid, sodium, or barium, and is potassium of niobic acid, or a salt of a rubidium.

[Claim 4] The photocatalyst system according to claim 2 or 3 in which said rare earth element is Eu, Ho, Er, or Tm.

[Claim 5] The photocatalyst system according to any one of claims 1 to 4 with which said photocatalyst contains a co-catalyst further.

[Claim 6] The photocatalyst system according to claim 5 in which said co-catalyst is Pt,  $\text{RuO}_2$ , Rh,  $\text{NiO}_x$ , or  $\text{CeO}_2$ .

Drawing:



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(54) 【発明の名称】 光触媒システム

(57) 【要約】

【課題】 可視光領域（波長が420 nm以上）や赤外光領域（波長が750 nm以上）の光の照射により光触媒効果を有する触媒システムを提供する

【解決手段】 従来紫外領域の光を使用していた光触媒を、可視・赤外光を紫外・可視光に変換する材料であるアップコンバージョン材料と組み合わせることによって、可視・赤外光領域で動作する光触媒系を組み立てる。即ち、本発明は、光触媒及びアップコンバージョン材料から成る光触媒システムである。

【特許請求の範囲】

【請求項1】 光触媒及びアップコンバージョン材料から成る光触媒システム。

【請求項2】 前記光触媒が、酸化チタン、チタン酸ストロンチウム、タンタル酸の金属塩、酸化タンタル、酸化ジルコニウム、及びニオブ酸の金属塩から成る群から選択される少なくとも2種を主成分とするものであり、前記アップコンバージョン材料がフッ化アルミニウム、フッ化インジウム、フッ化亜鉛、酸化ガリウム、及び酸化テルルから成る群から選択される少なくとも2種を主成分とし、これに希土類元素を含有させた請求項1に記載の光触媒システム。

【請求項3】 前記タンタル酸の金属塩がタンタル酸のカリウム、ナトリウム又はバリウムの塩であり、前記ニオブ酸の金属塩がニオブ酸のカリウム又はルビジウムの塩である請求項2に記載の光触媒システム。

【請求項4】 前記希土類元素がCe、Ho、Er、又はTmである請求項2又は3に記載の光触媒システム。

【請求項5】 前記光触媒が更に助触媒を含む請求項1〜4のいずれか一項に記載の光触媒システム。

【請求項6】 前記助触媒がPt、RuO<sub>4</sub>、Rh、NiO<sub>2</sub>、又はCeO<sub>2</sub>である請求項5に記載の光触媒システム。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、光触媒システムに関し、より詳細には、可視光や赤外光の照射により光触媒作用を有する光触媒システムに関する。

【0002】

【従来の技術】太陽光をエネルギー源として化学反応を触媒するために、数多くの光触媒材料が開発されており、そのいくつかはすでに実用化されている。これら実用化された光触媒は主に酸化チタンを主成分としており、したがって太陽光のうち強度の低い紫外光部分を主に利用している。太陽光中でより強度の大きい可視光を利用できる触媒材料も開発されているが、それらには毒性や動作中に材料自身が急速に変性してしまうなどの欠点があり、実用化にはなっていない。また赤外光領域の光照射により触媒反応を起こす光触媒材料はまだ見出されていない。

【0003】近年、太陽光をエネルギー源として化学反応を触媒するために、数多くの光触媒材料が開発されており、それらには、酸化チタン、酸化カドミウム、酸化亜鉛等々がある（「光が関与する触媒化学」化学総論No.2、日本化学会編（1994））。このうち酸化チタンを主成分としたものは抗菌剤や脱臭フィルターなどとして既に実用化されている（最新光触媒技術、エヌ・ティ・エス（2000））。酸化チタンはそのバンドギャップが3.0〜3.2 eVで、利用できる光の波長はほぼ400 nm以下の紫外光部分が主になっており、したがってこれら実用触媒の使用に際しては太陽光や蛍光灯に含まれるわず

かの量の紫外線や、また紫外線だけを出すブラックライトなどを使用している。最近では種々の改良の結果、この吸収域が可視光領域の500 nm近辺まで延びた酸化チタン系光触媒も開発されている（山下、実保、化学、52、74（1997））ものの、太陽光のかんりの部分を占める可視光領域を利用するにはまだ余地がある。また、可視光応答性のある触媒として知られる酸化カドミウムや硫化亜鉛なども、そのバンドギャップは約2.4 eVで、利用できる光は波長約550 nm以下のものであり、同じく可視光の全域を利用するには至っていない（これら可視光応答性のある光触媒は、上述したようにその毒性や使用中の劣化のために実用化はされていない）。また赤外光領域（波長が750 nm以上）で触媒反応を起こす触媒はまだ見出されていない。

【0004】一方、入射光を短波長の出力光に変換するアップコンバージョン技術が知られている（田部、平尾、虎溪、固体物理、27、185（1992））。これは結晶又はガラス中にドープされた希土類イオンのエネルギー準位を利用して近赤外線起光を可視又は紫外光に変換するものであり、2以上の長波長のフォトンが効率よく励起に関与して短波長の可視又は紫外の光を発することができ、このような観点から様々な組み合わせのアップコンバージョン材料が開発されている（特開2000-339735、特開平9-208947、特開平9-86958、特開平7-162062等）。

【0005】

【発明が解決しようとする課題】本発明は、可視光領域（波長が420 nm以上）や赤外光領域（波長が750 nm以上）の光の照射により光触媒効果を有する触媒システムを提供することを目的とする。また本発明は、従来太陽光のうち強度の低い紫外線領域の光を使用していた光触媒を、より強度の高い可視光領域ならびにこれまでに利用されていなかった赤外光領域で、安定かつ安全に使用できるようにする。

【0006】

【課題を解決するための手段】本発明においては、既に紫外光ならびに可視光の一部領域で使用されるその実用性能が確立されている、又は紫外光ならびに紫外光に近い可視光の一部領域で高活性を示すことがわかっている光触媒を、多光子過程により可視・赤外光を紫外・可視光に変換する材料であるアップコンバージョン材料と組み合わせ、可視・赤外光領域で動作する光触媒系を組み立てた。

【0007】即ち、本発明は、光触媒及びアップコンバージョン材料から成る光触媒システムである。この光触媒は、酸化チタン、チタン酸ストロンチウム、タンタル酸の金属塩、酸化タンタル、酸化ジルコニウム、及びニオブ酸の金属塩から成る群から選択される少なくとも1種を主成分とするものであり、このアップコンバージョン材料がフッ化アルミニウム、フッ化インジウム、フッ





2) 上記の1)の反応を速くさせるための材料(例えば、光触媒、排水浄化材、大気浄化材、脱臭・抗菌・防汚などの機能を有する光触媒塗材等)として用いる。  
3) 太陽電池の電極材として用いる。

【0015】

【実施例】以下、実施例にて本発明を例証するが、本発明を限定することを意図するものではない。

【実施例1】

本実施例においては、各種光源を用いて大気中窒素酸化物除去反応における本発明の光触媒システムの触媒作用を調べた。光触媒として、チタン酸インプロボキンドを加水分解して調製して得た酸化チタン( $\text{TiO}_2$ )粉末を用いた。アップコンバージョン材料として、各成分を溶融混合して調製して得たトリウム含有フッ化アルミニウム系ガラス( $40\text{AlF}_3 \cdot 22\text{CaF}_2 \cdot 22\text{BaF}_2 \cdot 15\text{YF}_3 \cdot 1\text{ThF}_4$ )粉末を用いた。これらの光触媒粉末とアップコンバージョン材料の粉末とを各0.1g混合したものを石英製の角型反応管(断面横1cm<sup>2</sup>、長さ10cm)の底部に設置し、それに室温で一酸化窒素( $\text{NO}$ )を1ppm含む空気を0.2リットル/分流通させ、反応管上部より200Wキセノンランプ光を照射し、この反応管とキセノン\*

\*ランプの間に適宜波長選択フィルターを設置した。この試験における各装置の配置を図1に示す。

【0016】試験は、(1)コントロールとして光を全く当てない場合(「照射光なし」と表す。)、(2)フィルターを用いないでキセノンランプを照射した場合(「前光照射」と表す。)、(3)フィルターとして、580nm以下の光の透過率が0%で、かつ630nm以上の光の透過率が92%であるシャープカットフィルターを通してキセノンランプ光を照射した場合(「フィルター1」と表す。)、及び(4)フィルターとして、720nm以下の光の透過率が0%で、かつ820nm以上の光の透過率が90%であるシャープカットフィルターを通してキセノンランプ光を照射した場合(「フィルター2」と表す。の4通りで行った。試験後のNOの減少量を反応率として赤外吸収法により測定した。

【0017】比較例1

アップコンバージョン材料を用いない以外は実施例1と同様に測定を行った。実施例1と比較例1との測定結果を表1に示す。

【表1】

|      | 反応率(%) |      |        |        |
|------|--------|------|--------|--------|
|      | 照射光なし  | 全光照射 | フィルター1 | フィルター2 |
| 実施例1 | 0      | 13   | 3.8    | 1.8    |
| 比較例1 | 0      | 14   | 0      | 0      |

【0018】比較例1においては、紫外光照射下では光触媒( $\text{TiO}_2$ )だけで(アップコンバージョン材料がなくとも)試験反応は進行するが、可視光や赤外光ではまったく反応しない。ところが実施例1においてはアップコンバージョン材料を光触媒と共存させると、紫外光はもとより、可視光や赤外光でも反応が進行した。

【0019】実施例2

本実施例においては、実施例1と同様の各種光源を用いて、メタノールを犠牲試薬とする水の分解反応における本発明の光触媒システムの触媒作用を調べた。光触媒として、実施例1の酸化チタンに白金塩を含浸保持して調製した白金担持酸化チタン( $\text{Pt/TiO}_2$ )粉末を用いた。アップコンバージョン材料として、トリウム含有フッ化※

※インジウム系ガラス( $38\text{InF}_3 \cdot 19\text{BaF}_2 \cdot 15\text{ZnF}_2 \cdot 10\text{PbF}_2 \cdot 10\text{SrF}_2 \cdot 2\text{AlF}_3 \cdot 2\text{CaF}_2 \cdot 22\text{BaF}_2 \cdot 0.1\text{ThF}_4$ )粉末を各成分を溶融混合して調製して用いた。これらの光触媒粉末とアップコンバージョン材料の粉末を各1gを反応液(メタノール10%水溶液)中に懸濁させ、そこに実施例1と同様にキセノンランプ光を照射し、発生する水素の量をガスクロマトグラフ法により測定した。

【0020】比較例2

アップコンバージョン材料を用いない以外は実施例2と同様に測定を行った。実施例2と比較例2との測定結果を表2に示す。

【表2】

|      | 水素発生量(μmol) |      |        |        |
|------|-------------|------|--------|--------|
|      | 照射光なし       | 全光照射 | フィルター1 | フィルター2 |
| 実施例2 | 0           | 612  | 25     | 5      |
| 比較例2 | 0           | 815  | 0      | 0      |

比較例2においては、紫外光照射下では光触媒( $\text{Pt/TiO}_2$ )だけで(アップコンバージョン材料がなくとも)試験反応は進行するが、可視光や赤外光ではまったく反応しない。ところが実施例2においては、アップコンバージョン材料を光触媒と共存させると、紫外光はもとより、可視光や赤外光でも反応が進行した。

【図面の簡単な説明】

【図1】実施例で用いた装置の配置を示す図である。

【符号の説明】

- 1 光触媒システム
- 2 石英製角型反応器
- 3 フィルター

4 キセノンランプ

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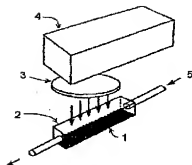
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\* \* 5 反応ガス

【図1】



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